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In re Application of:

Callant et al.

Art Unit: Unassigned

Application No. 10/657,931

Examiner: Unassigned

Filed: September 9, 2003

For: n-TYPE METAL OXIDE SEMICONDUCTOR SPECTRALLY
SENSITIZED WITH A CATIONIC SPECTRAL SENSITIZER

CLAIM OF PRIORITY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

In accordance with the provisions of 35 USC 119, Applicants claim the priority of the following application:

Application No. PCT/EP02/10269, filed in the European Patent
Office on September 12, 2002.

A certified copy of the above-listed priority document is enclosed.

Respectfully submitted,

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Date: October 7, 2003

CERTIFICATE OF MAILING

I hereby certify that this CLAIM OF PRIORITY (along with any documents referred to as being attached or enclosed) is being deposited with the United States Postal Service on the date shown below with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Date: 10/7/03



Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten internationalen Patentanmeldung überein.

The attached documents are exact copies of the international patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet international spécifiée à la page suivante.

Den Haag, den
The Hague,
La Haye, le

25. 09. 2003

Der Präsident des Europäischen Patentamts
Im Auftrag
For the President of the European Patent Office
Le Président de l'Office européen des brevets
p. o.

Désirée Vrolijk

Patentanmeldung Nr.
Patent application no. PCT/EP 02/10269
Demande de brevet n°

**Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation**



Anmeldung Nr.:
Application no.: PCT/EP 02/10269
Demande n°:

Anmelder:
Applicant(s): 1. AGFA-GEVAERT - Mortsel, Belgium
Demandeur(s):

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention: N-TYPE METAL OXIDE SEMICONDUCTOR SPECTRALLY SENSITIZED
WITH A CATIONIC SPECTRAL SENSITIZER

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PCT REQUEST

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V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZM ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE BG CH&LI CY CZ DE DK EE ES FI FR GB GR IE IT LU MC NL PT SE SK TR and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GQ GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&LI CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ OM PH PL PT RO RU SD SE SG SI SK SL TJ TM TN TR TT TZ UA UG UZ VC VN YU ZA ZM ZW

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n-TYPE METAL OXIDE SEMICONDUCTOR SPECTRALLY SENSITIZED WITH A
CATIONIC SPECTRAL SENSITIZER

Field of the invention

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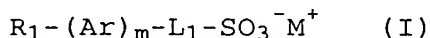
The present invention relates to nano-porous n-type metal oxide semiconductor spectrally sensitized with a cationic spectral sensitizer.

10 Background of the invention.

The foundations of dye-sensitized semiconductors as an electrochemical means for light energy conversion were laid in the 1970's [see Gerischer, Photochem. Photobiol., volume 16, pages 243-
15 260 (1972)] and developed into application of a dye-sensitized film to an electrode [see T. Miyasaka et al., Nature, volume 277, pages 638-640 (1979)]. Use of an aggregate of fine semiconductor particles having a large surface area available for dye adsorption had been proposed to bring about considerably improved light
20 capturing efficiency, which has made it feasible to apply dye-sensitized semiconductor to a wet type solar cell. In particular, a wet type solar cell having a nano-porous film of dye-sensitized titanium dioxide semiconductor particles as a work electrode has been expected to surpass an amorphous silicon solar cell in
25 conversion efficiency and cost. These fundamental techniques were disclosed in 1991 by Graetzel et al. in Nature, volume 353, pages 737-740 and in US 4,927,721, US 5,350,644 and JP-A 05-504023. In order to increase further the solar conversion efficiency of solar cells, it is important to increase the photocurrent
30 photoefficiency. One approach is to improve the adsorption of dye sensitizers on the semiconductor layer.

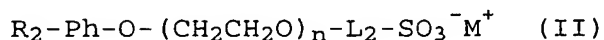
EP-A 1 137 022 discloses semiconductor particles having a dye adsorbed thereby in the presence of an anionic sulfonic acid derivative, preferably represented by formula (I):

35



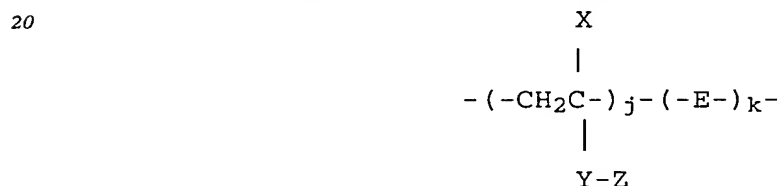
wherein R_1 represents a hydrogen atom or a substituted or unsubstituted alkyl group; Ar represents a substituted or
40 unsubstituted arylene group; m represents 0 or 1; L_1 represents a single bond or a divalent linking group; and M^+ represents a

cation; provided that a combination of a hydrogen atom as R_1 , 0 as m , and a single bond L_1 is excluded; or by formula (II):



5 wherein R_2 represents a straight chain or branched alkyl group; Ph represents a phenylene group; n represents an integer of 0 to 50; L_2 represents a single bond, a substituted or unsubstituted alkylene group or a substituted or unsubstituted alkyleneoxy group;
10 and M^+ represents a cation.

JP-A 2001-024252 discloses a photo-electric conversion material containing a semiconductor sensitized with a pigment or dye whose adsorption thereon is assisted by a compound A represented by general formula (I): $R-L-Z$, wherein R is an
15 optionally substituted alkyl, alkenyl or aryl group; L is a single bond or a divalent linking group; and Z is an acidic group (which dissociates a proton), or its alkali metal salt. Furthermore, the photo-electric conversion material may also contain a high molecular weight polymer B represented by general formula (II):



25 wherein X is a hydrogen atom or a C_{1-4} alkyl group; Y is a single bond or a divalent linking group; E is a repeat unit derived from a compound with ethylenic unsaturation; Z is an acidic group (which dissociates a proton), or its alkali metal salt; and j, k are the weight composition ratio of the repeat units. Preferred acidic
30 groups which dissociate a proton are carboxylic acid and sulfonic groups, although boric acid, phenolic and hydroxy groups are also mentioned. All the specific compounds according to formula (I) disclosed in JP-A 2001-024252 have a carboxy group as their acidic group which dissociates a proton and several compounds have more
35 than one carboxy group.

In 2000 Rice et al. reported in the New Journal of Chemistry, volume 24, pages 651-652, that catechol was an efficient anchoring group for attachment of ruthenium-polypyridine photosensitizers to solar cells based on nanocrystalline titanium dioxide films, the
40 formation of surface titanium-catecholate complexes in aqueous media having been previously reported by Borgias et al. [see Inorganic Chemistry, volume 23, 1009 (1984)] and Rodriguez et al.

[see J. Colloidal and Interface Science, volume 177, pages 122-131 (1996)] and the formation of an interfacial charge transfer complex between catechol and titanium dioxide particles having been previously reported by Liu et al. [see J. Phys. Chem. B, volume 5 103, pages 2480-2486 (1999)]. Moreover, in 1993 Redmond et al. had established that the adsorption of pyrocatechol on the surface of a transparent nanocrystalline titanium dioxide film altered the dependence of the rate constant for accumulation on the initially applied potential in a manner consistent with energetic promotion 10 of the intraband surface state, associated with incompletely coordinated Ti atoms at the surface of the nanocrystalline titanium dioxide film, into the conduction band.

A critical feature of photovoltaic devices based on nano-porous titanium dioxide is their spectral sensitization, which in 15 large measure determines their efficiency. Organic metal complex dyes (preferably including ruthenium) usually show a very fast electron injection in the titanium dioxide semiconductor upon light excitation. Pure anionic organic dye compounds (e.g. merocyanines) also exhibit very fast electron injection in the TiO_2 semiconductor 20 upon light excitation. Spectral sensitization of titanium dioxide semiconductors with cationic dye sensitizers is, to our knowledge, unknown.

There is therefore a need for enhanced spectral dye sensitization of n-type metal oxide semiconductors and for methods 25 to achieve enhanced spectral sensitization of nano-porous n-type metal oxide semiconductors with dyes. Furthermore, there is also a need for a means of using cationic dye sensitizers for the sensitization of n-type metal oxide semiconductors.

30 Aspects of the invention.

It is therefore an aspect of the present invention to provide a layer configuration in which a n-type metal oxide semiconductor layer is efficiently spectrally sensitized with a cationic dye 35 sensitizer.

It is a further aspect of the present invention to provide a process for achieving efficient spectral sensitization of a n-type metal oxide semiconductor with a cationic dye sensitizer.

It is also an aspect of the present invention to provide a 40 cationic dye-sensitized photovoltaic device which achieves a high short circuit current.

It is also an aspect of the present invention to provide a cationic dye-sensitized solar cell which achieves a high conversion efficiency.

Further aspects and advantages of the invention will become
5 apparent from the description hereinafter.

Summary of the invention.

It has been surprisingly found that by coadsorbing cationic
10 dye sensitizers with certain ortho-dihydroxy-benzene compounds, such as 3,4,5-trihydroxy-benzonitrile and 3,4-dihydroxy-benzonitrile, on nano-porous n-type metal oxide semiconductors, that the adsorption of the cationic dyes is enhanced together with their sensitization efficiency. This can be achieved by first
15 adsorbing the ortho-dihydroxy-benzene compound and then adsorbing the cationic dye sensitizer or by adsorbing the ortho-dihydroxy-benzene compound and the cationic dye sensitizer simultaneously.

Aspects of the present invention are realized by a layer configuration comprising a layer of a nano-porous n-type metal
20 oxide semiconductor with a band-gap of greater than 2.7 eV, an adsorbed cationic spectral sensitizer and a coadsorber capable of enhancing the adsorption of a cationic spectral sensitizer on a n-type metal oxide semiconductor.

Aspects of the present invention are also realized by a
25 photovoltaic device comprising the above-mentioned layer configuration.

Aspects of the present invention are also realized by a solar cell comprising the above-mentioned layer configuration.

Aspects of the present invention are also realized by a
30 process for preparing the above-mentioned layer configuration comprising the steps of: providing a layer of a nano-porous n-type metal oxide semiconductor with a band-gap of greater than 2.7 eV, adsorbing the coadsorber on the nano-porous n-type metal oxide semiconductor layer and adsorbing a cationic spectral sensitizer on
35 the n-type metal oxide semiconductor layer.

Preferred embodiments are disclosed in the dependent claims.

Detailed description of the invention.

Definitions

The term nano-porous metal oxide semiconductor means a metal oxide semiconductor having pores with a size of 100 nm or less and
5 having an internal surface area of at least 20 m²/g and not more than 300 m²/g.

The term anionic spectral sensitizer means a dye with an overall negative charge having spectral sensitizing properties, such as cyanine dyes with at least two covalently-bonded acidic
10 group either as a free acid or as a salt and merocyanine dyes with at least one covalently-bonded acidic group either as a free acid or as a salt. Covalently bonded acidic groups include a hydroxy group on an aromatic ring system and sulpho [-SO₃], sulphato [-O-SO₃], carboxy [-CO₂] and phosphoric acid groups. Anionic dyes
15 exhibit an ionic interaction with positively charged sites on surfaces, such as on certain natural and artificial fibres.

The term cationic spectral sensitizer means a dye with an overall positive charge having spectral sensitizing properties, such as merocyanine dye with at least one covalently-bonded
20 positively charged group, such as a quaternary ammonium group or a ternary sulfonium group, and cyanine dyes. Cationic dyes exhibit an ionic interaction with negatively charged sites on surfaces, such as on certain natural and artificial fibres.

The term ortho-dihydroxy-benzene compound includes 1,2-
25 dihydroxybenzene, also known as cathechol, and substituted ortho-dihydroxy-benzene compounds, such substitution also including carbocyclic and heterocyclic rings systems annelated (i.e. sharing two carbon atoms) with a ortho-dihydroxy-benzene nucleus for example aromatic and heteroaromatic ring systems.

30 The term alkyl means all variants possible for each number of carbon atoms in the alkyl group i.e. for three carbon atoms: n-propyl and isopropyl; for four carbon atoms: n-butyl, isobutyl and tertiary-butyl; for five carbon atoms: n-pentyl, 1,1-dimethyl-propyl, 2,2-dimethylpropyl and 2-methyl-butyl etc.

35 The term "support" means a "self-supporting material" so as to distinguish it from a "layer" which may be coated on a support, but which is itself not self-supporting. It also includes any treatment necessary for, or layer applied to aid, adhesion to the support.

40 The term continuous layer refers to a layer in a single plane covering the whole area of the support and not necessarily in direct contact with the support.

The term non-continuous layer refers to a layer in a single plane not covering the whole area of the support and not necessarily in direct contact with the support.

5 Nano-porous metal oxide semiconductor

Aspects of the present invention are provided by a layer configuration comprising a layer of a nano-porous n-type metal oxide semiconductor with a band-gap of greater than 2.7 eV, an
10 adsorbed cationic spectral sensitizer and a coadsorber capable of enhancing the adsorption of a cationic spectral sensitizer on a n-type metal oxide semiconductor.

According to a first embodiment of the layer configuration, according to the present invention, the n-type metal oxide
15 semiconductor is selected from the group consisting of titanium oxides, tin oxides, niobium oxides, tantalum oxides and zinc oxides.

According to a second embodiment of the layer configuration, according to the present invention, the n-type metal oxide
20 semiconductor is titanium dioxide.

For efficient solar cells, the coating of the nano-porous TiO₂ should be between 8 and 12 μm in order to have sufficient light absorption for generating power conversion efficiencies up to 5 to 8%. The thicker the titanium dioxide coating, the longer the
25 pathway for the charges (electrons) have to be transported to the charge collecting electrode and the greater the probability of recombination occurring with resultant power conversion efficiency loss. In order to circumvent this problem smaller titanium dioxide nano-particles can be used, having a larger specific surface and
30 hence enabling thinner layers to be realized with the same light absorbance values. In this way, photovoltaic cells with higher efficiencies can be obtained due to the fact that the probability of recombination is reduced due to the path traversed by the electrons to the charge collecting electrode being shorter.

35 The metal oxide semiconductor nano-particles with a band-gap of greater than 2.7 eV used in the process, according to the present invention, can be prepared by wet precipitation and non-wet-precipitation processes. Non-wet-precipitation processes include such processes as the flame pyrolysis process operated by
40 DEGUSSA. Titanium dioxide nano-particles produced according to wet-chemical process are commercially available from SOLARONIX SA as Ti-Nanoxide™ T, a nano-sized titanium dioxide with a mean

particle size of 13 nm and a specific surface of 120 m²/g, and Ti-Nanoxide™ HT, a nano-sized titanium dioxide with a mean particle size 9 nm and specific surface of 165 m²/g, which are often used as n-type semi-conductor nano-particles in making Graetzel-type
5 photovoltaic cells, or can be readily synthesized using fairly straightforward precipitation techniques as disclosed in 1997 by Barbe et al. in the Journal of the American Ceramic Society, volume 80 (12), pages 3157 - 3171, herein incorporated by reference.

According to a third embodiment of the layer configuration,
10 according to the present invention, the metal oxide is titanium dioxide prepared by a non-wet-precipitation process.

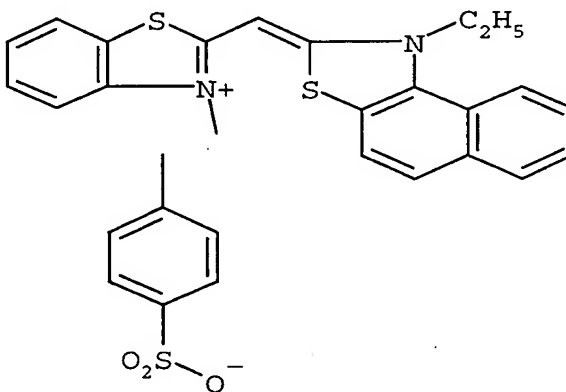
Cationic spectral sensitizers

15 Aspects of the present invention are provided by a layer configuration comprising a layer of a nano-porous n-type metal oxide semiconductor with a band-gap of greater than 2.7 eV, an adsorbed cationic spectral sensitizer and a coadsorber capable of enhancing the adsorption of a cationic spectral sensitizer on a n-
20 type metal oxide semiconductor.

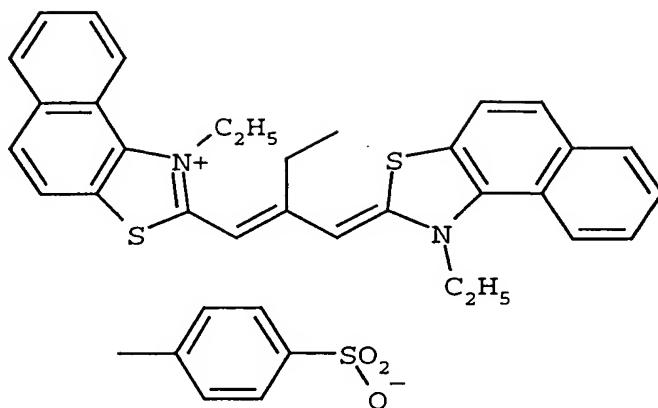
According to a fourth embodiment of the layer configuration, according to the present invention, the cationic spectral sensitizer is a cyanine dye.

Cationic spectral sensitizers suitable for use in the present
25 invention include:

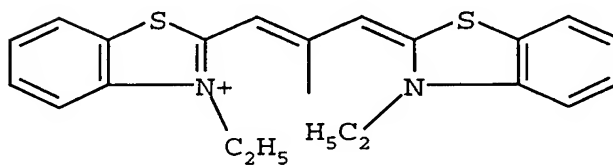
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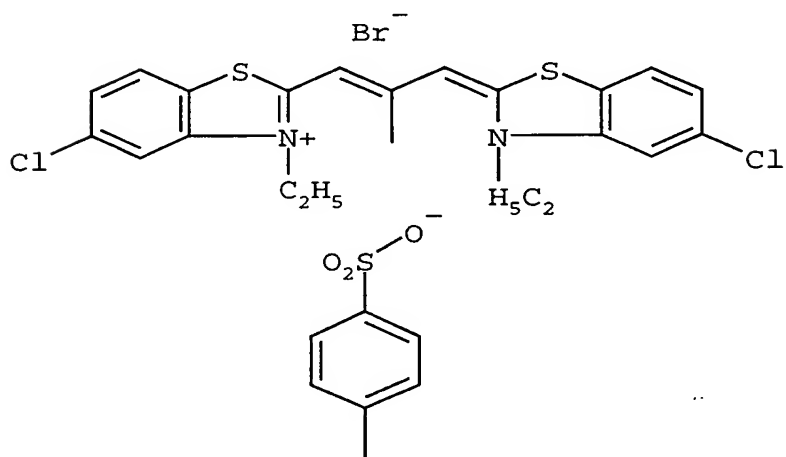
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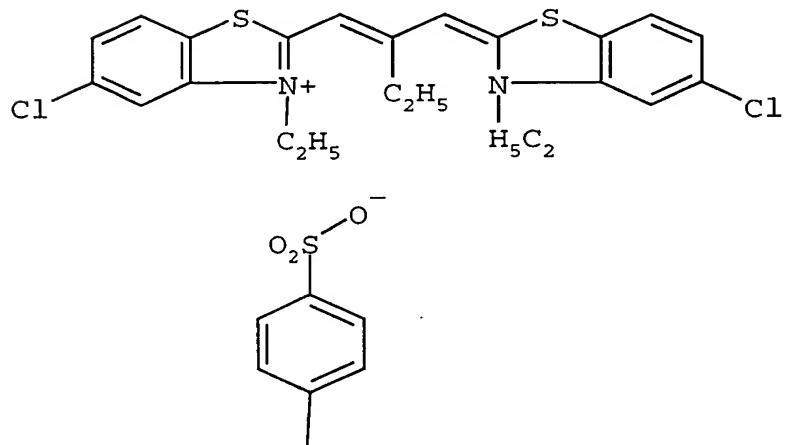
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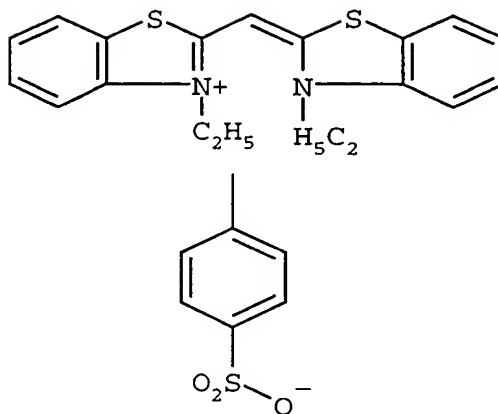


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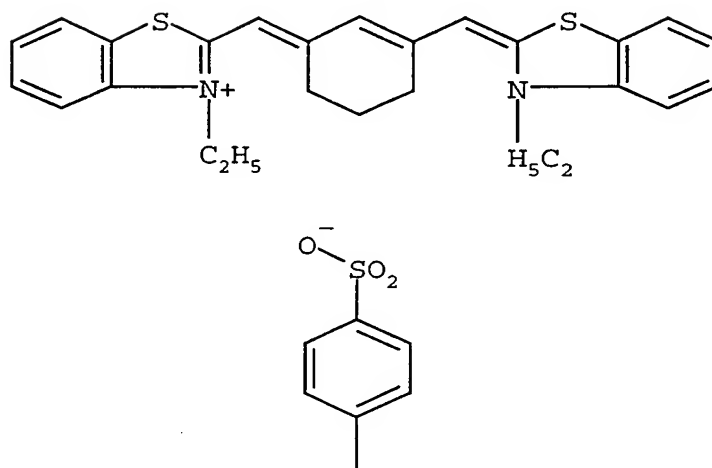


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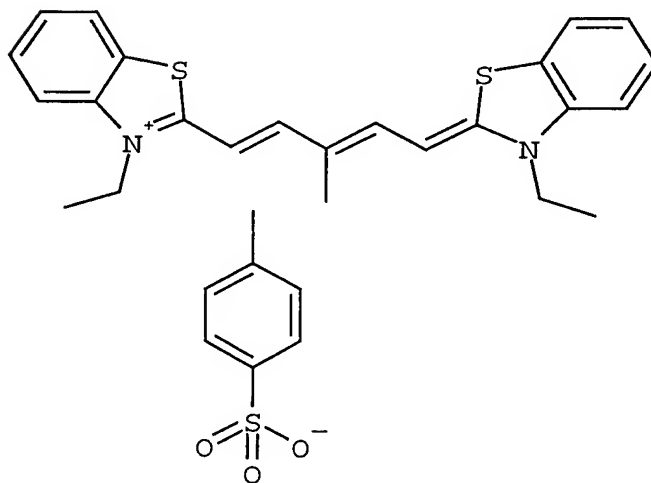
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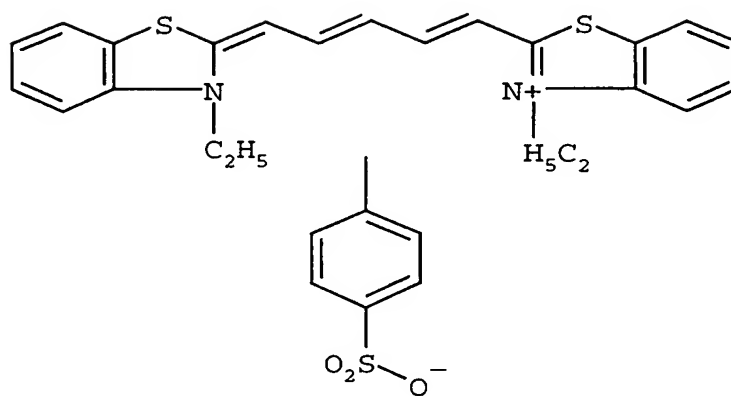


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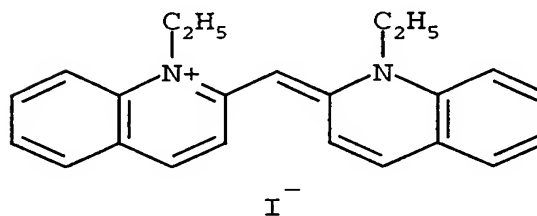


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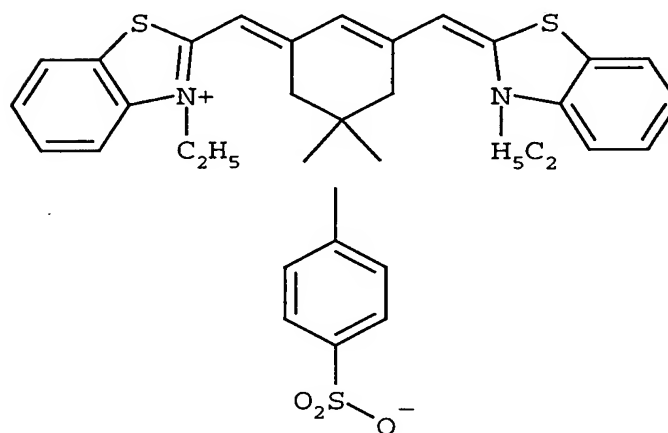
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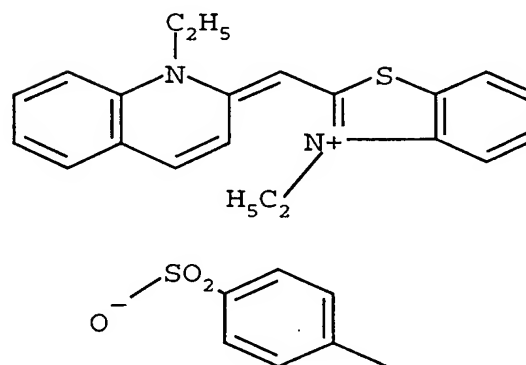
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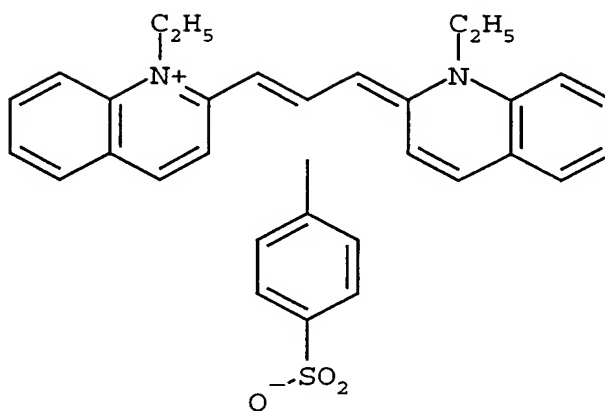


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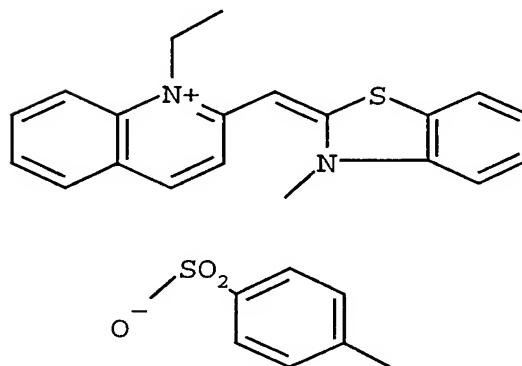


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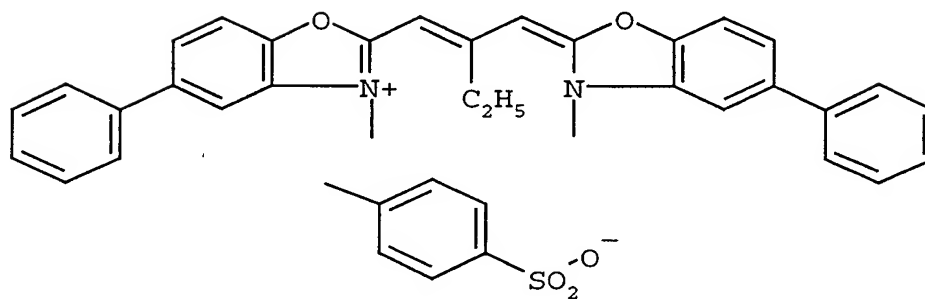
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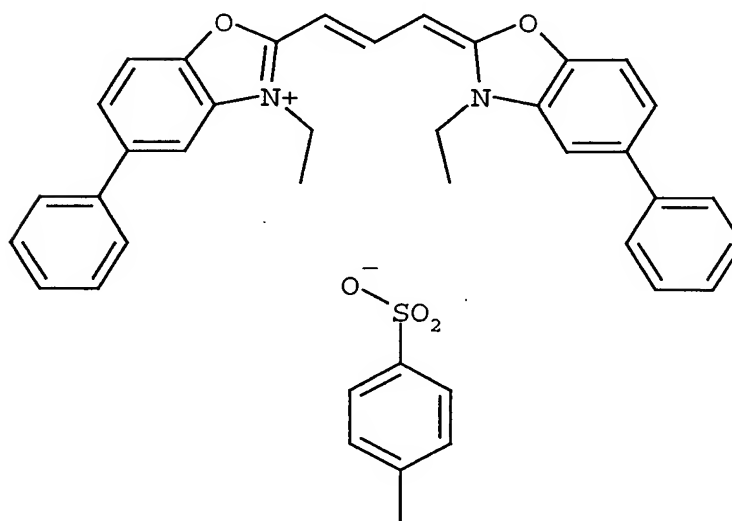
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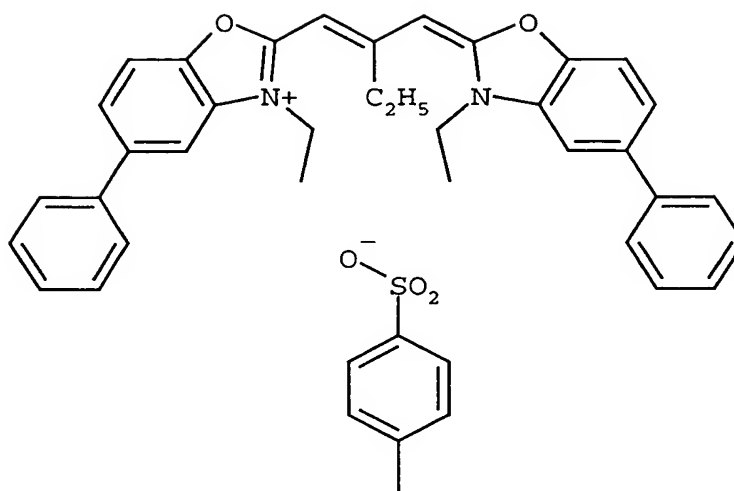


DC-16



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DC-17



Coadsorber

Aspects of the present invention are provided by a layer
 5 configuration comprising a layer of a nano-porous n-type metal
 oxide semiconductor with a band-gap of greater than 2.7 eV, an
 adsorbed cationic spectral sensitizer and a coadsorber capable of
 enhancing the adsorption of a cationic spectral sensitizer on a n-
 type metal oxide semiconductor.

10 According to a fifth embodiment of the layer configuration,
 according to the present invention, the coadsorber is an ortho-
 dihydroxy-benzene compound.

According to a sixth embodiment of the layer configuration,
 according to the present invention, the coadsorber is an ortho-
 15 dihydroxy-benzene compound with a group having a Hammett σ value of
 at least 0.60 and below 1.00.

According to a seventh embodiment of the layer configuration,
 according to the present invention, the coadsorber is an ortho-
 dihydroxy-benzene compound with a group having a Hammett σ value of
 20 at least 0.60 and below 1.00, wherein the ortho-dihydroxy-benzene
 compound has the ortho-dihydroxy-groups and the group having a
 Hammett σ value of at least 0.60 and below 1.00 on the same benzene
 ring.

According to an eighth embodiment of the layer configuration,
 25 according to the present invention, the coadsorber is an ortho-
 dihydroxy-benzene compound with a nitrile group substituted on the
 same benzene ring as the ortho-dihydroxy-groups.

According to a ninth embodiment of the layer configuration,
 according to the present invention, the coadsorber is selected from

the group consisting of 2,3-dihydroxy-benzonitrile, 3,4-dihydroxy-benzonitrile, 3,4,5-trihydroxy-benzonitrile, 3,4-dihydroxy-4'-cyano-benzophenone, 4-nitro-catechol, (3,4-dihydroxy-phenyl)methylsulphone, 1,2-dihydroxy-anthraquinone, 3,4-dihydroxy-anthraquinone-2-sulphonic acid, 4,5-dihydroxy-benzene-1,3-disulphonic acid, 6,7-dihydroxy-naphthalene-2-sulphonic acid, 3,4-dihydroxy-benzoic acid and catechol.

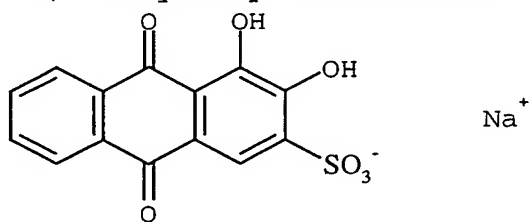
According to a tenth embodiment of the layer configuration, according to the present invention, the coadsorber is selected from the group consisting of 3,4-dihydroxy-benzonitrile, 3,4,5-trihydroxy-benzonitrile, 1,2-dihydroxy-anthraquinone, (3,4-dihydroxy-phenyl)methylsulphone, 4,5-dihydroxy-benzene-1,3-disulphonic acid and catechol.

Coadsorbers suitable for use in the present invention include:

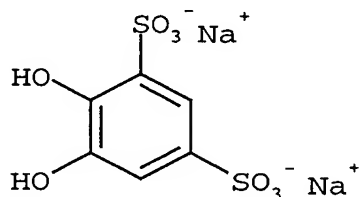
CA-01

3,4-dihydroxy-benzonitrile

CA-02



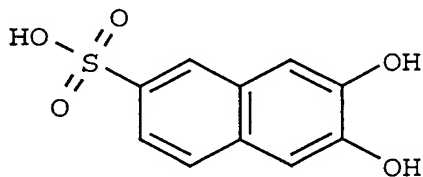
CA-03



CA-04

1,2-dihydroxy-anthraquinone

CA-05



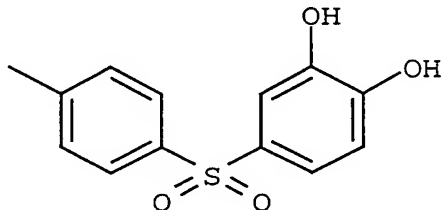
CA-06

ethyl 3,4-dihydroxybenzoate

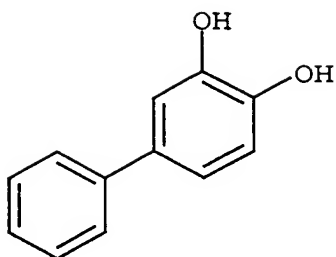
CA-07

3,4-dihydroxy-benzophenone

CA-08



CA-09



- CA-10 2,3-dihydroxy-benzonitrile
CA-11 3,4,5-trihydroxy-benzonitrile
CA-12 3,4-dihydroxy-4'-cyano-benzophenone
CA-13 4-nitro-catechol
CA-14 (3,4-dihydroxy-phenyl)methylsulphone
CA-15 3,4-dihydroxy-benzoic acid
CA-16 catechol

Process for preparing a layer configuration

Aspects of the present invention are realized by a process for
5 preparing a layer configuration, according to the present
invention, comprising the steps of: providing a layer of a nano-
porous n-type metal oxide semiconductor with a band-gap of greater
than 2.7 eV, adsorbing a coadsorber on the nano-porous n-type metal
oxide semiconductor layer and adsorbing a cationic spectral
10 sensitizer on the nano-porous n-type metal oxide semiconductor
layer.

According to a first embodiment of the process for preparing a
layer configuration, according to the present invention, the
adsorption of the cationic spectral sensitizer on the nano-porous
15 n-type metal oxide semiconductor layer is carried out
simultaneously with the adsorption of the coadsorber on the nano-
porous n-type metal oxide semiconductor layer. When applied from
the same solution it is possible that complex formation between the
coadsorber and the cationic spectral sensitizer takes place before
20 adsorption on the nano-porous n-type metal oxide semiconductor
layer i.e. that a complex is adsorbed rather than the two
components individually.

According to a second embodiment of the process for preparing a
layer configuration, according to the present invention, the
25 adsorption of the cationic spectral sensitizer on the nano-porous
n-type metal oxide semiconductor layer is carried out after the
adsorption of the coadsorber on the nano-porous n-type metal oxide
semiconductor layer.

Support

Supports for use according to the present invention include
5 polymeric films, silicon, ceramics, oxides, glass, polymeric film
reinforced glass, glass/plastic laminates, metal/plastic laminates,
paper and laminated paper, optionally treated, provided with a
subbing layer or other adhesion promoting means to aid adhesion to
the light-exposure differentiable element. Suitable polymeric films
10 are poly(ethylene terephthalate), poly(ethylene naphthalate),
polystyrene, polyethersulphone, polycarbonate, polyacrylate,
polyamide, polyimides, cellulose triacetate, polyolefins and
poly(vinylchloride), optionally treated by corona discharge or glow
discharge or provided with a subbing layer.

15

Photovoltaic devices

Aspects of the present invention are also realized by a
photovoltaic device comprising the layer configuration, according
20 to the present invention, or produced according to the process,
according to the present invention.

Photovoltaic devices incorporating the spectrally sensitized
nano-porous n-type metal oxide semiconductor, according to the
present invention, can be of two types: the regenerative type which
25 converts light into electrical power leaving no net chemical change
behind in which current-carrying electrons are transported to the
anode and the external circuit and the holes are transported to the
cathode where they are oxidized by the electrons from the external
circuit and the photosynthetic type in which there are two redox
30 systems one reacting with the holes at the surface of the
semiconductor electrode and one reacting with the electrons
entering the counter-electrode, for example, water is oxidized to
oxygen at the semiconductor photoanode and reduced to hydrogen at
the cathode. In the case of the regenerative type of photovoltaic
35 cell, as exemplified by the Graetzel cell, the hole transporting
medium may be a liquid electrolyte supporting a redox reaction, a
gel electrolyte supporting a redox reaction, an organic hole
transporting material, which may be a low molecular weight material
such as 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-
40 spirobifluorene (OMeTAD) or triphenylamine compounds or a polymer
such as PPV-derivatives, poly(N-vinylcarbazole) etc., or inorganic
semiconductors such as CuI, CuSCN etc. The charge transporting

process can be ionic as, for example, in the case of a liquid electrolyte or gel electrolyte or electronic as, for example, in the case of organic or inorganic hole transporting materials.

Such regenerative photovoltaic devices can have a variety of
5 internal structures in conformity with the end use. Conceivable forms are roughly divided into two types: structures which receive light from both sides and those which receive light from one side. An example of the former is a structure made up of a transparently conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer
10 and a transparent counter electrode electrically conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer having interposed therebetween a photosensitive layer and a charge transporting layer. Such devices preferably have their sides sealed with a polymer, an adhesive etc. to prevent deterioration or
15 volatilization of the inside substances. The external circuit connected to the electrically-conductive substrate and the counter electrode via the respective leads is well-known.

Alternatively the spectrally sensitized nano-porous n-type metal oxide semiconductor, according to the present invention, can
20 be incorporated in hybrid photovoltaic compositions such as described in 1991 by Graetzel et al. in Nature, volume 353, pages 737-740, in 1998 by U. Bach et al. [see Nature, volume 395, pages 583-585 (1998)] and in 2002 by W. U. Huynh et al. [see Science, volume 295, pages 2425-2427 (2002)]. In all these cases, at least
25 one of the components (light absorber, electron transporter or hole transporter) is inorganic (e.g. nano-TiO₂ as electron transporter, CdSe as light absorber and electron transporter) and at least one of the components is organic (e.g. triphenylamine as hole transporter or poly(3-hexylthiophene) as hole transporter).

30

Industrial application

Layer configurations, according to the present invention, can be used in photovoltaic devices and solar cells.

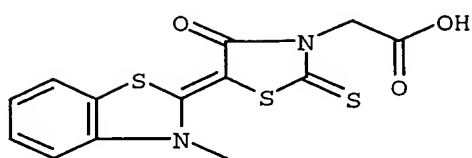
35

The invention is illustrated hereinafter by way of reference and invention light emitting devices. The percentages and ratios given in these examples are by weight unless otherwise indicated.

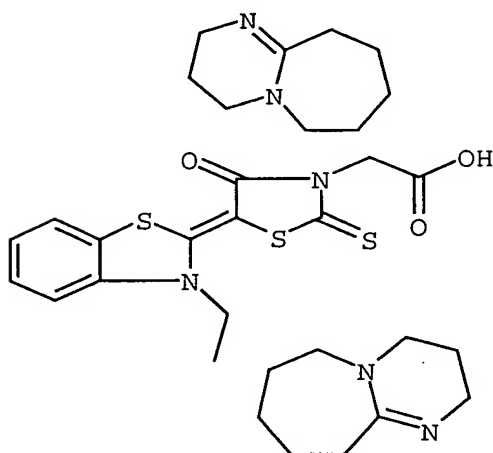
40 Anionic spectral sensitizers used in the comparative experiments:

17

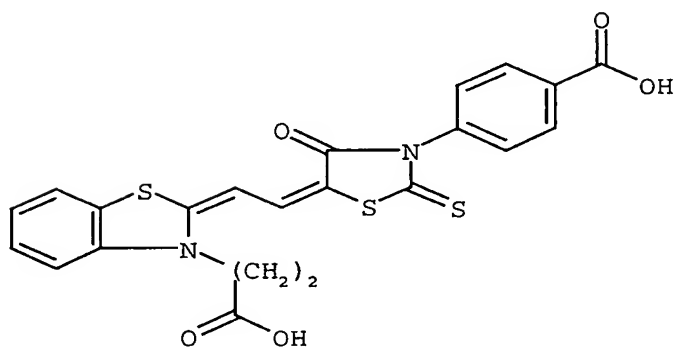
DA-01



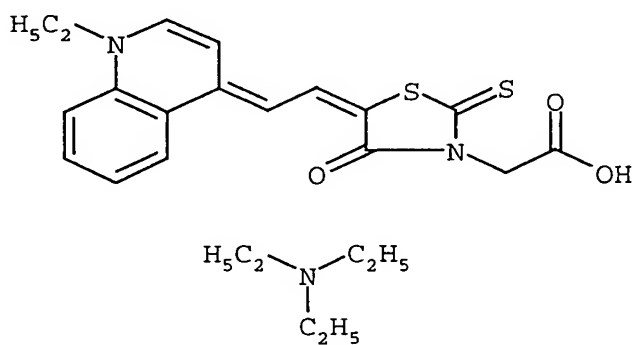
DA-02



DA-03

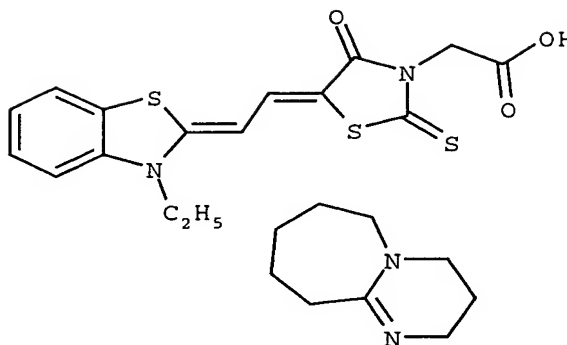


DA-04



18

DA-05



EXAMPLE 1

Adsorption of dyes on a nano-porous TiO₂ layer

5

A glass substrate (FLACHGLAS AG) was ultrasonically cleaned in ethanol for 5 minutes and then dried. A layer of a nano-TiO₂ dispersion (Ti-nanoxide HT from Solaronix SA) was applied to the glass substrate using a doctor blade coater. This titanium dioxide-coated glass was heated to 450°C for 30 minutes. This results in a highly transparent nano-porous TiO₂ layer. A dry layer thickness of 1.5 µm, 3 µm or 5 µm, as verified by laserprofilometry (DEKTRAK™ profilometer), mechanically with a diamond-tipped probe (Perthometer) and interferometry, was obtained depending on the doctor blade knife used.

After this sintering step, the titanium dioxide-coated glass plates were cooled to 150°C by placing it on a hot plate at 150°C for 10 minutes and then immediately immersed in a dye-containing solution optionally containing an ortho-dihydroxy-benzene compound where they remained for 15 to 17 hours. After immersion in the dye solution, the titanium dioxide layers were rinsed with acetonitrile to remove non-adsorbed dye and then dried at 50°C for several mins.

Absorption spectra between 200 and 800 nm were obtained using a Hewlett-Packard diode-array spectrophotometer HP 8452A. The results are given in Table 1 for adsorption of the cationic dyes and reference spectra of the dyes in acetonitrile.

Table 1:

Comparative experiment nr	Cationic dye	λ_{\max} of dye solution [nm]	λ_{\max} of dyed TiO ₂ -layer [nm]	Absorbance at λ_{\max} of dyed TiO ₂ -layer
1	DC-01	440	-	0.4 (color lost)
2	DC-02	586	-	-
3	DC-03	543	-	-
4	DC-04	548	-	-
5	DC-05	548	-	-
6	DC-06	426	-	0.2 (color lost)
7	DC-07	644	-	0.6 (color lost)
8	DC-08	650	-	0.8 (color lost)
9	DC-09	654	-	0.6 (color lost)
10	DC-10	524	-	0.6 (color lost)
11	DC-11	648	-	0.7 (color lost)
12	DC-12	484	-	0.7 (color lost)
13	DC-13	604	-	0.4 (color lost)
14	DC-14	484	-	0.18 (color lost)
15	DC-15	500	-	-
16	DC-16	498	-	-
17	DC-17	502	-	-

Immersion of the freshly sintered titanium dioxide layers in 2×10^{-4} M solutions of the cationic dyes, DC-01 to DC-17, in acetonitrile for 15 to 17 hours, resulted in no detectable dye adsorption after washing with acetonitrile.

The absorption results for coadsorption of the cationic dyes with an ortho-dihydroxy-benzene compound according to the present invention are given in Table 2.

Table 2:

Invention experiment nr.	Cationic dye	Coadsorber	λ_{\max} of cationic dye solution [nm]	λ_{\max} of dyed TiO ₂ -layer [nm]	Absorbance at λ_{\max} of dyed TiO ₂ -layer
1	DC-01	CA-01	440	424	0.77
2	DC-02	CA-01	586	597	0.38
3	DC-03	CA-01	543	549	0.24
4	DC-04	CA-01	548	554	0.24
5	DC-05	CA-01	548	559	0.17
6	DC-06	CA-01	426	426	0.72
7	DC-07	CA-01	644	663	1.1
8	DC-08	CA-01	650	650	1.0
9	DC-09	CA-01	654	654	1.0
10	DC-10	CA-01	524	526	0.67

11	DC-11	CA-01	648	648	0.65
12	DC-12	CA-01	484	486	0.41
13	DC-13	CA-01	604	608	0.90
14	DC-14	CA-01	484	456	0.39
15	DC-15	CA-01	500	500	0.86
16	DC-16	CA-01	498	502	0.85
17	DC-17	CA-01	502	508	0.71
18	DC-02	CA-02	586	586	0.33#
19	DC-02	CA-03	586	594	0.48
20	DC-02	CA-04	586	590	0.20
21	DC-03	CA-04	543	553	0.40*
22	DC-04	CA-04	550	564	0.35*
23	DC-05	CA-04	583	560	0.32*
24	DC-02	CA-05	586	586	0.25
25	DC-02	CA-06	586	586	0.19
26	DC-03	CA-06	543	550	0.17
27	DC-04	CA-06	548	551	0.15
28	DC-02	CA-07	586	586	0.14
29	DC-03	CA-07	543	550	0.26
30	DC-04	CA-07	548	553	0.18
31	DC-05	CA-07	548	552	0.23
32	DC-02	CA-08	586	586	0.31
33	DC-03	CA-08	543	550	0.28
34	DC-04	CA-08	548	553	0.28
35	DC-05	CA-08	548	552	0.25
36	DC-02	CA-09	586	586	0.26
37	DC-03	CA-09	543	550	0.27
38	DC-04	CA-09	548	553	0.22
39	DC-01	CA-11	440	422	1.47
40	DC-02	CA-11	576	592	0.96
41	DC-15	CA-11	500	516	1.46
42	DC-01	CA-14	440	416	0.69
43	DC-15	CA-14	500	505	0.35
44	DC-01	CA-15	440	419	0.34
45	DC-15	CA-15	500	508	0.17
46	DC-01	CA-16	440	417	0.53
47	DC-02	CA-16	576	580	0.20
48	DC-15	CA-16	500	504	0.21

corrected for absorbance of CA-02 on titanium dioxide

* corrected for absorbance of CA-04 on titanium dioxide

Immersion of the freshly sintered titanium dioxide layers in acetonitrile solutions 2×10^{-4} M in cationic dye (DC-01 to DC-17) and 2×10^{-4} M in coadsorber compounds CA-01 to CA-09, CA-11, C-14 to C-16 respectively resulted in detectable dye adsorption.

Particularly strong adsorption was observed with cationic dyes with coadsorbers CA-01, CA-03, CA-04, CA-11, CA-14 and CA-15.

It should also be noted that no difference in dye adsorption was observed when coadsorber CA-01 was adsorbed on the titanium dioxide layer from a 2×10^{-4} M acetonitrile solution of CA-01 by immersion for 15 to 17 hours as described for the dye solutions, washed with acetonitrile, dried at 50°C for several minutes before immersion for 15 to 17 hours in a 2×10^{-4} M acetonitrile solution of DC-01, DC-02 and DC-11, washing with acetonitrile and finally drying at 50°C for several minutes.

By way of reference five anionic dyes were adsorbed on the TiO₂-surface (1.5 µm thickness): DA-01, DA-02, DA-03, DC-04 and DC-05 using the same procedure as for the cationic dyes. The results of these adsorption experiments are shown in Table 4.

It can be concluded from the results given in Table 4, that comparable light absorption can be attained on nano-porous titanium dioxide with cationic spectral sensitizers in association with the coadsorber, according to the present invention, to that attainable with anionic spectral sensitizers.

Table 4:

Comparative experiment nr	Anionic dye	λ_{\max} of anionic dye solution [nm]	λ_{\max} of dyed TiO ₂ -layer [nm]	Absorbance at λ_{\max} of dyed TiO ₂ -layer
18	DA-1	430	420	1.75
19	DA-2	426	420	1.45
20	DA-3	500	500	1.63
21	DA-4	610	580	1.95
22	DA-5	520	500	1.45

EXAMPLE 2

Influence of molar ratio of coadsorber to cationic spectral sensitizer on absorbance of adsorbed spectral sensitizer on TiO₂

Invention experiments 41 to 50 were carried out as described for Invention experiments 16 and 17 except that the concentrations of DC-16, DC-17 and CA-01 were varied as given in Table 5.

Table 5:

Invention experiment nr.	Cationic dye		CA-01 concentration in adsorbing CH ₃ CN solution [M]	Absorbance at λ_{\max} of dyed TiO ₂ -layer
	type	concentration [M] in adsorbing CH ₃ CN solution		
41	DC-16	1.5×10^{-4}	0.5×10^{-4}	0.93
42	DC-16	1.0×10^{-4}	1.0×10^{-4}	0.88
43	DC-16	0.66×10^{-4}	1.34×10^{-4}	0.85
44	DC-16	0.5×10^{-4}	1.5×10^{-4}	0.83
45	DC-16	0.2×10^{-4}	1.8×10^{-4}	0.61
46	DC-17	1.5×10^{-4}	0.5×10^{-4}	0.93
47	DC-17	1.0×10^{-4}	1.0×10^{-4}	0.87
48	DC-17	0.66×10^{-4}	1.34×10^{-4}	0.80
49	DC-17	0.5×10^{-4}	1.5×10^{-4}	0.71
50	DC-17	0.2×10^{-4}	1.8×10^{-4}	0.52

The results given in Table 5 show that the adsorption of cationic dyes in the presence of CA-01 increased strongly with CA-01 concentration for both DC-16 and DC-17 i.e. a higher absorbance on titanium dioxide was observed at a dye concentration of 5×10^{-5} M and a CA-01 concentration of 1.5×10^{-4} M than at a dye concentration of 1×10^{-4} M and a CA-01 concentration of 1×10^{-4} M.

10

EXAMPLE 3

Evaluation in photovoltaic devices

Photovoltaic devices 1 to 8 were prepared as follows:

Preparation of the front electrode

A glass plate ($2 \times 7 \text{ cm}^2$) coated with conductive SnO₂:F (Pilkington TEC15/3) with a surface conductivity of ca 15 Ohm/square was ultrasonically cleaned in isopropanol for 5 minutes and then dried.

The electrode was taped off at the borders and was doctor blade-coated in the middle ($0.7 \times 4.5 \text{ cm}^2$) with the above-described Solaronix disperion of TiO₂ to give layer thicknesses after sintering of 1.8 or 5 μm to ensure comparable optical absorbances of the cells. The sintering procedure and cationic spectral sensitizer adsorption procedure in the presence of a coadsorber were as described for EXAMPLE 1. The front electrode was thereby produced, which was immediately used in assembling the cell.

25

Cell assembly

The back electrode (consisting of $\text{SnO}_2\text{:F}$ glass (Pilkington TEC15/3) evaporated with platinum to catalyse the reduction of the electrolyte) was sealed together with the front electrode with two pre-patterned layers of Surlyn® (DuPont) ($2 \times 7 \text{ cm}^2$ where in the middle $1 \times 6 \text{ cm}^2$ had been removed) in between. This was performed at a temperature just above 100°C on a hotplate. As soon as the sealing was completed, the cell was cooled to 25°C and electrolyte was added through holes in the counter electrode. The electrolyte used was a solution of 0.5 M LiI, 0.05 M I_2 and 0.4 M t-butylpyridine in acetonitrile and was injected into the cell during cell assembly. The holes were then sealed with Surlyn® and a thin piece of glass. Conductive tape was attached on both long sides of the cell to collect the electricity during measurement.

Device characterisation

The cell was irradiated with a Steuernagel Solar Constant 575 solar simulator with a metal halide 1 AM light source. The simulator was adjusted to about 1 sun equivalent. The generated electricity was recorded with a Keithley electrometer (Type 2400 SMU). The open circuit voltage (V_{oc}), short circuit current density (I_{sc}) and Fill Factor (FF) of the photocell calculated from the quantity of electricity generated are shown in table 6.

Table 6:

Device nr.	Dye	Co-adsorber	TiO ₂ thickness [μm]	λ_{max} [nm]	Absorbance at λ_{max}	I_{sc} [mA/cm^2]	V_{oc} [V]	FF
1 (comp.)	DA-01	-	1.8	420	1.20	1.65	0.440	0.49
2 (comp.)	DA-02	-	1.8	420	1.30	1.8	0.485	0.48
3 (comp.)	DA-03	-	1.8	500	2.22	1.25	0.507	0.56
4 (comp.)	DA-04	-	1.8	580	1.98	0.25	0.132	0.40
5 (comp.)	DA-05	-	1.8	500	1.15	1.2	0.397	0.51
6 (inv.)	DC-01	CA-01	5.0	440	2.20	1.9	0.525	0.59
7 (inv.)	DC-02	CA-01	5.0	590	1.85	1.7	0.515	0.59
8 (inv.)	DC-02	CA-02	5.0	590	1.30	0.6	0.400	0.54

The results in Table 6 show that comparable short circuit currents [I_{sc}] can be realized with cationic dye sensitization in the presence of a coadsorber as can be obtained with anionic dye sensitization, especially if the dye absorbs in the red region of the visible spectrum.

EXAMPLE 4

Spectral sensitization with mixtures of cationic spectral sensitizers

To broaden the spectral response of photovoltaic devices based on spectral sensitization of nano-porous titanium dioxide with cationic spectral sensitizers with a coadsorber capable of enhancing the adsorption thereof, a mixture of cationic dyes was used together with the coadsorber CA-01.

Photovoltaic cells were prepared as described in EXAMPLE 3 with the cationic spectral sensitizers separately and with a mixtures of the cationic spectral sensitizers. For these experiments Degussa P25 TiO_2 nano-colloid, a nano-titanium dioxide produced by a non-wet-precipitation process i.e. by flame pyrolysis, was used instead of the Ti-nanoxide HT from Solaronix, a nano-titanium dioxide produced by a wet-precipitation process, 5 g of Degussa P25 being added to 15 mL of water with 1 mL of Triton X-100 being subsequently added. The resulting titanium dioxide colloidal dispersion was cooled in ice and ultrasonically treated for 5 minutes. This titanium dioxide colloidal dispersion was then further used as described above for the Ti-nanoxide HT dispersion.

The dye adsorption was carried out with a cationic spectral sensitizer concentration of 1×10^{-4} M and a CA-1 concentration of 1×10^{-4} M for the three cationic spectral sensitizers and with a mixture of 0.5×10^{-4} M CA-01, 0.3×10^{-4} M DC-01, 0.7×10^{-4} M DC-15 and 0.5×10^{-4} M DC-02. If equal amounts of the three dyes were used, an inhomogeneous spectrum resulted due to the differences in adsorption strength of the cationic spectral sensitizers. The relative amounts of the dyes were therefore adapted to realize a homogeneous absorption throughout the visible spectrum.

The thereby prepared photovoltaic cells were irradiated with a Xenon Arc Discharge lamp with a power of 100 mW/cm^2 . The current generated was recorded with a Keithley electrometer (Type 2420). The open circuit voltage (V_{oc}), short circuit current density (I_{sc})

and Fill Factor (FF) of the photocell as calculated from the quality of generated current are given in Table 7.

Table 7.

5

Device nr.	Dye	Coadsorber	TiO ₂ thickness [μm]	λ _{max} [nm]	Absorbance at λ _{max}	I _{sc} [mA/cm ²]	V _{oc} [V]	FF
9	DC-01	CA-01	2.0	430	1.08	1.71	0.470	0.41
10	DC-15	CA-01	2.0	508	0.92	1.93	0.570	0.57
11	DC-02	CA-01	2.0	588	0.98	1.35	0.460	0.51
12	DC-01, DC-15, DC-02	CA-01	2.0	430 508 588	0.45 0.50 0.49	1.96	0.600	0.38

As can be seen from Table 7, although the absorbance values for the dye mixture are half of the values for the dyes adsorbed separately, comparable or higher short circuit current values were
 10 obtained due to the broader spectral response.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any
 15 generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

CLAIMS

1. A layer configuration comprising a layer of a nano-porous n-type metal oxide semiconductor with a band-gap of greater than 2.7 eV, an adsorbed cationic spectral sensitizer and a coadsorber capable of enhancing the adsorption of a cationic spectral sensitizer on a n-type metal oxide semiconductor.
2. Layer configuration according to claim 1, wherein said coadsorber is an ortho-dihydroxy-benzene compound.
3. Layer configuration according to claim 2, wherein said benzene compound with a nitrile group substituted on the same benzene ring as said ortho-dihydroxy-groups.
4. Layer configuration according to claim 1, wherein said coadsorber is selected from the group consisting of 2,3-dihydroxy-benzonitrile, 3,4-dihydroxy-benzonitrile, 3,4,5-trihydroxy-benzonitrile, 3,4-dihydroxy-4'-cyano-benzophenone, 4-nitro-catechol, (3,4-dihydroxy-phenyl)methyl-sulphone, 1,2-dihydroxy-anthraquinone, 3,4-dihydroxy-anthraquinone-2-sulphonic acid, 4,5-dihydroxy-benzene-1,3-disulphonic acid, 6,7-dihydroxy-naphthalene-2-sulphonic acid, 3,4-dihydroxy-benzoic acid and catechol.
5. Layer configuration according to claim 1, wherein said coadsorber is selected from the group consisting of 3,4-dihydroxy-benzonitrile, 3,4,5-trihydroxy-benzonitrile, 1,2-dihydroxy-anthraquinone, (3,4-dihydroxy-phenyl)methylsulphone, 4,5-dihydroxy-benzene-1,3-disulphonic acid and catechol.
6. Layer configuration according to claim 1, wherein said cationic spectral sensitizer is a cyanine dye.
7. A photovoltaic device comprising a layer configuration comprising a layer of a nano-porous n-type metal oxide semiconductor with a band-gap of greater than 2.7 eV, an adsorbed cationic spectral sensitizer and a coadsorber capable of enhancing the adsorption of a cationic spectral sensitizer on a n-type metal oxide semiconductor.

8. A solar cell comprising a layer configuration comprising a layer of a nano-porous n-type metal oxide semiconductor with a band-gap of greater than 2.7 eV, an adsorbed cationic spectral sensitizer and a coadsorber capable of enhancing the adsorption of a cationic spectral sensitizer on a n-type metal oxide semiconductor.
9. A process for preparing a layer configuration, comprising a layer of a nano-porous n-type metal oxide semiconductor with a band-gap of greater than 2.7 eV, an adsorbed cationic spectral sensitizer and a coadsorber capable of enhancing the adsorption of a cationic spectral sensitizer on a n-type metal oxide semiconductor, comprising the steps of: providing a layer of a nano-porous n-type metal oxide semiconductor with a band-gap of greater than 2.7 eV, adsorbing a coadsorber on said nano-porous n-type metal oxide semiconductor layer and adsorbing a cationic spectral sensitizer on said nano-porous n-type metal oxide semiconductor layer.
10. Process according to claim 9, wherein said adsorption of said cationic spectral sensitizer on said nano-porous n-type metal oxide semiconductor layer is carried out simultaneously with said adsorption of said coadsorber on said nano-porous n-type metal oxide semiconductor layer.
11. Process according to claim 9, wherein said adsorption of said cationic spectral sensitizer on said nano-porous n-type metal oxide semiconductor layer is carried out after said adsorption of said coadsorber on said nano-porous n-type metal oxide semiconductor layer.

ABSTRACT

n-TYPE METAL OXIDE SEMICONDUCTOR SPECTRALLY SENSITIZED WITH A
CATIONIC SPECTRAL SENSITIZER

5

A layer configuration comprising a layer of a nano-porous n-type metal oxide semiconductor with a band-gap of greater than 2.7 eV, an adsorbed cationic spectral sensitizer and a coadsorber capable of enhancing the adsorption of a cationic spectral sensitizer on an
10 n-type metal oxide semiconductor; and a process for preparing this layer configuration comprising the steps of: providing a layer of a nano-porous n-type metal oxide semiconductor with a band-gap of greater than 2.7 eV, adsorbing a coadsorber on the nano-porous n-type metal oxide semiconductor layer and adsorbing a cationic
15 spectral sensitizer on the nano-porous n-type metal oxide semiconductor layer.